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(54) Title: TOUGHENED, HIGH-MODULUS POLYACETALS

(57) Abstract: A composition and method for forming a polyacetal composition of molded articles that exhibit desirable combinations of stiffness and impact resistance, wherein the composition contains a mineral filler.



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TITLE

TOUGHENED, HIGH-MODULUS POLYACETALS

FIELD OF THE INVENTION

This invention relates to a polyacetal composition for molded articles
 5 exhibiting desirable combinations of stiffness and impact resistance. More particularly, this invention relates to a composition comprising a polyacetal and a mineral filler.

TECHNICAL BACKGROUND OF THE INVENTION

Polyacetals are well known in the art, and are in widespread commercial
 10 use, principally in the form of polyoxymethylene homopolymer and copolymers. Polyoxymethylene homopolymer is generally formed by polymerizing formaldehyde or trioxane, the cyclic ether form of formaldehyde. Copolymers are generally formed by combining formaldehyde with various cyclic ethers such as ethylene oxide or 1,3-dioxolane to form a polymer chain having two or more
 15 methylene groups directly adjacent to one another, thereby improving the thermal stability over that of the homopolymer. See for example U.S. Patent 2,768,994, U.S. Patent 3,027,352.

Polyacetal homopolymers and copolymers have been modified in various ways in order to broaden the spectrum of available properties. Representative are
 20 the modifications to Delrin® homopolymer, available from DuPont, as shown in Table 1. Table 1 shows commercially available grades of polyacetal homopolymer which have been modified in order to provide combinations of stiffness and toughness not available from unmodified polyacetal homopolymer. Stiffness is indicated by the flexural modulus determined according to ASTM
 25 D790, and toughness is indicated by notched Izod impact resistance determined according to ASTM D256.

Table 1 Properties of Commercial Polyacetal Homopolymer Resins			
Delrin® Resin	Description	Flexural Modulus (ASTM D790) MPa (Ksi)	Izod Impact Resistance (ASTM D256) J/m(ft-lbs/in)
500	unmodified	3110 (450)	76 (1.4)
500T	toughened	2250 (330)	128 (2.4)
100ST	toughened	1130 (160)	840 (16)
525GR	glass reinforced	8000 (1160)	96 (1.8)

With continuing reference to Table 1, blending short glass fibers in a polyacetal resin composition (e.g., Delrin® 525GR) provides about 130% improvement in toughness and about a 300% increase in stiffness over the Delrin® 500. However, glass fibers significantly reduce the moldability of the resulting resin and may lead to property anisotropy, uneven shrinkage, and part warpage. Mineral fillers provide similar improvements in stiffness to the polyacetal resin but usually with a reduction in toughness, even though processibility and product isotropy are improved over a glass containing composition.

It is known in the art to incorporate fatty acids, particularly stearic acid, into mineral filled polyolefin compositions. For example, U.S. Patent No. 4,795,768 to Ancker et al. discloses a composition consisting of high density polyethylene filled with 50 wt-% of a 3.5 μm CaCO_3 pre-treated with 2% by weight of isostearic acid. Izod impact was decreased by about 8% with respect to the unfilled polymer while flexural modulus was increased by about 150%.

Orange, 10th Int. Conf. Deformation, Yield, and Fracture of Polymers, Inst. of Mat., pp. 502ff, (1997) discloses filled polypropylene compositions containing 10% by volume of a 0.1 μm and 2 μm CaCO_3 both stearic acid treated and untreated. The compositions containing the stearic acid treated fillers exhibited fracture toughness higher than the unfilled polymer and somewhat higher stiffness. The composition containing the 2 μm untreated filler was similar to the treated composition, but that containing the 0.1 μm untreated filler exhibited a 50% reduction in fracture toughness and about a 45% increase in stiffness.

Suetsugu, The Polymer Processing Society, (1990), discloses an increase of notched Izod impact resistance of 230% in a high molecular weight polypropylene composition containing 30% by weight of stearic acid treated 4.3 μm CaCO_3 .

The differences between saturated and unsaturated fatty acids in their interaction with mineral particles is disclosed in Ottewill et al., *J. Oil Colour Chemists Assn*, 50:844 (197).

Flexman in Toughened Plastics I, C. Keith Riew and Anthony J. Kinloch, editors, American Chemical Society, Washington, 1993, shows that the fracture mechanics of polyacetals differs considerably from that of polyamides.

SUMMARY OF THE INVENTION

In one aspect of the present invention, there is provided a composition comprising a polyoxymethylene polymer comprising up to 10 mol-% of repeat units comprising oxyalkylene radicals having adjacent methylene units, about 1%-30% by volume of a mineral filler having an aspect ratio (the average ratio of the largest to the smallest dimension of the filler particle) of 5 or less, the filler

having an average equivalent spherical diameter in the range of about 0.1 to less than about 3.5 micrometers, and a saturated organic acid, salt thereof, or a mixture thereof, at a concentration of at least about 0.5% by weight of the mineral filler.

In another aspect, the invention relates to a process for forming a composition, comprising the steps of combining a polyoxymethylene polymer comprising up to 10 mol-% of repeat units comprising oxyalkylene radicals having adjacent methylene units, with a mineral filler having an aspect ratio of less than 5, the mineral filler having an average equivalent spherical diameter in the range of about 0.1 to about 3.5 micrometers, and a saturated organic acid, salt thereof, or a mixture thereof, at a concentration of at least about 0.5% by weight of the mineral filler, the mineral filler and the polyacetal being combined at a weight ratio given by the formula:

$$W_f/W_p = [VF/(1-VF)] \cdot D_f/D_p$$

where W_f is the weight of the filler, W_p is the weight of the polymer, VF is the desired volume fraction of filler, in the range of about 0.01-0.3, D_f is the density of the filler, and D_p is the density of the polymer.

heating the combination to a temperature above the melting point of the polyacetal to form a molten composition;

mixing the molten composition to provide a homogenous melt; and, cooling the molten composition.

DETAILED DESCRIPTION

This invention, through the incorporation of saturated organic acids, salts thereof, or mixtures thereof, into compositions comprising polyacetals and mineral fillers, results in improvements in properties over the unfilled polymer and filled polymers containing impact modifiers of the art. This invention increases stiffness at constant or increased toughness over the unmodified resin.

Polyacetal homopolymers, and copolymers formed from two or more aldehyde or cyclic ether monomers are suitable for the practice of the present invention including those which have been nucleated, pigmented, and otherwise modified according to practices common in the art. The polyacetals of this invention may include small amounts of common additives, typically less than 5% by weight, which may affect toughness or stiffness, including: stabilizers, antioxidants, mold release agents, lubricants, glass fibers, carbon black, plasticizers, pigments, and other well-known additives commonly employed in the art.

Polyacetals preferred for the practice of the present invention include polyoxymethylene homopolymer, or a copolymer thereof comprising up to 10 mol-% of alkylene radical repeat units having adjacent methylene groups.

Preferred copolymers include those formed by copolymerizing according to the teachings of the art formaldehyde or trioxane with cyclic ethers having 2-12 carbon atoms, preferably 1,3-dioxolane. Preferably said alkylene radical repeat units represent no more than 5 mol-%, most preferably not more than 2 mol-%, of the total polymer. Preferred polyoxymethylene copolymers are dipolymers of formaldehyde and ethylene oxide where the quantity of ethylene oxide incorporated into the polymer is about 2 weight percent. The preferred polyoxymethylene homo- and copolymers for use in the compositions of the present invention are those with a number average molecular weight of about 20,000 to 100,000, more preferably 20,000 to 80,000 and most preferably 25,000 to 70,000 and those whose terminal hydroxyl groups have been end-capped by a chemical reaction to form ester or ether groups, preferably acetate or methoxy groups, respectively according to the teachings in U.S. Patent 2,768,994, *op.cit.*

Suitable inorganic fillers for use in this invention are those that do not have significant off-gassing or decompose themselves or cause polyacetal to decompose at typical polyacetal processing conditions, including the time-temperature combinations of injection molding. These include, but are not limited to: calcium carbonate; oxides such as alumina, silica, and titanium dioxide; sulfates such as barium sulfate; titanates; kaolin clay and other silicates; magnesium hydroxide, and carbon black. In the present invention, an aspect ratio (the average ratio of the largest to the smallest dimension of the filler particle) of less than about 5 avoids stress concentrations and part anisotropies. The preferred fillers are calcium carbonate and titanium dioxide.

The size of the filler particles is stated as the equivalent spherical diameter. The equivalent spherical diameter is the diameter of a sphere having the same volume as the filler particle and may be determined by use of a Sedigraph 5100 (Micrometrics Instrument Corporation, Norcross, GA). The Sedigraph 5100 determines particle size by the sedimentation method, measuring the gravity-induced settling rates of different size particles in a liquid with known properties. The rate at which particles fall through the liquid is described by Stokes' Law. The largest particles fall fastest, while the smallest particles fall slowest. The sedimentation rate is measured using a finely collimated beam of low energy X-rays which pass through the sample cell to a detector. The distribution of particle mass at various points in the cell affects the number of X-ray pulses reaching the detector. This X-ray pulse count is used to derive the particle size distribution expressed as the percent mass at given particle diameters. Since particles rarely exhibit uniform shapes, each particle size is reported as an

“Equivalent Spherical Diameter”, the diameter of a sphere of the same material with the same speed of sedimentation.

Suitable particles have equivalent spherical diameters in the range of about 0.1 to less than about 3.5 micrometers, most typically about 0.5-2 micrometers.

5 The size of the filler particles can affect the toughness and/or stiffness properties of the composition of the invention. Particles that are either too large or too small do not produce the benefits of the present invention. A suitable filler particle has a relatively narrow size distribution with particular emphasis on having a minimum number of particles much larger than the mean particle size.

10 It is believed that the improvements provided by the invention are related to achieving a distance distribution with a mean value in the range of about 0.1 μm - about 1.0 μm ; controlling of the interface between resin and filler, and maintaining continuity of the polymer phase. The nearest neighbor interparticle separation is controlled by the combination of filler size, filler loading, and
15 adequate deagglomeration and dispersion of the filler. The polymer/filler interface is controlled by the use of sufficient but not excessive amounts of the saturated organic acids and/or salts of the invention. The continuity of the polymer phase is determined by the volume loading of filler.

20 The relationship among mean nearest neighbor interparticle distance (IPD), filler size, d , and required filler loading, ϕ (as a volume fraction), is given approximately by the equation

$$\text{IPD} = d \cdot [(\pi/6\phi)^{1/3} - 1].$$

For example, it was found thereby that when the interparticle separation is taken to be 0.3 μm the maximum particle size cannot exceed 20 μm at volume fractions
25 less than 0.50. When the particles occupy about 50% by volume or more, however, the continuity of the polymer matrix is jeopardized. At particle sizes at or below about 0.1 micrometer, the required interparticle separation range is readily achieved at volume loadings well-below 50% provided that the particles can be deagglomerated and homogeneously dispersed which can be very difficult
30 to achieve because of the very high surface forces binding the fine particles together. Also, it is believed that the toughening effect observed in the practice of this invention depends upon the efficient debonding of the filler particle from the resin during impact deformation. The ability to debond decreases with particle size. It is therefore believed that at particle sizes much below 0.1 micrometers,
35 the conditions are no longer favorable for debonding, making these particles sizes unsuitable.

It is believed that the polymer/filler interfacial forces are mediated by one or more saturated organic acids or salts thereof. The requisite amount depends

upon the interfacial area -- e.g., the greater the interfacial area, the more organic acid or acid salt is required. The actual amount however will depend upon the size and shape of the particles and the volume loading of the particles.

It is found that the concentration of filler varies with filler size, increasing
5 with increasing size in the suitable range. Thus, if the filler size is at the high end of the range, a higher concentration of filler is needed than if the filler size is at the lower end of the range. The suitable range is about 1 to about 30 vol. %, preferably about 5 to about 20 vol %, and most preferably about 10 to about 20 vol %. One of skill in the art, will recognize, however, that at 1% filler
10 loadings, polyacetal compositions will exhibit minimal improvements in stiffness or impact resistance.

At filler loadings greater than approximately 30 vol %, it becomes increasingly difficult to achieve a homogeneous distribution of non-agglomerated filler within the polymer matrix using ordinary methods of melt mixing.

15 Suitable saturated organic acids include aliphatic carboxylic acids having about 3-30 carbon atoms optionally substituted by one or more oxygen atoms or sulfur atoms. A suitable acid may optionally contain one or more aliphatic, aromatic, or functionalized side chains. Preferred organic acids include stearic acid. Inorganic salts of the suitable acids are equally suitable, including zinc
20 stearate and the like. It is understood by one of skill in the art that an organic acid in combination with a mineral at elevated temperatures may form a salt therewith so that the acid added to the mixture in the process of the invention may or may not be present in the final product thereof. The organic acids or salts thereof are present at a concentration of at least 0.5% by weight on the weight of the filler.
25 While there is no particular upper limit to concentration of organic acid, in one embodiment of the invention the concentration of organic acid or salt thereof is in the range of about 0.5-to about 4% by weight on the weight of the filler.

It is believed that a useful concentration of acid or acid salt in the composition of the invention corresponds to that at which the acid or salt forms a
30 molecular monolayer on substantially all of the mineral filler surface. Any amount less than that will exhibit less than the optimal combination of properties while any amount more than that serves no function except to dilute the amount of polymer in the composition. The addition of about 2% by weight of stearic acid on the weight of the 0.7 μm CaCO_3 is optimal.

35 The composition of the invention is formed by coating a filler with a saturated organic acid or salt thereof, mixing the coated filler into the polyacetal, and pelletizing the product. The saturated organic acids or salts may be, but are not required to be, applied to the filler in a separate coating step prior to

processing with polymer. In a method, known in the art, for applying organic acid or salt coatings to mineral fillers, the acid or salt is dissolved in an appropriate solvent and mixed with the filler until it is all coated. The thus coated filler can then be separated from the solution and the remaining solvent removed by drying.

5 In another method, the acid or acid salt, the filler and the polymer are combined at once. Mixing may further be achieved by dispersing the filler into a dispersion or solution of the polymer and the organic acid or salt thereof, followed by drying; Mixing may also be achieved in the melt, either in a batch mixer or a continuous extruder.

10 Preferably, the ingredients are dry-blended by tumbling followed by feeding to an extruder or batch mixer according to well-established methods of the art. Alternatively, the ingredients can be separately and continuously fed to one or more extruder zones by, for example, the use of weight loss feeders, all of the mixing being performed in the extruder; or the material may be added at once or
15 in stages to a batch type melt blender and the composition formed therein.

In one embodiment of the invention, the ingredients are processed in a twin-screw co-rotating extruder to ensure good mixing. The extrudate is pelletized and subsequently molded into parts by injection molding. The pellets can also be compression molded or a molded or extruded sheet can be
20 thermoformed into a complex shape. Other means known in the art may also be employed to form shaped articles of the composition of the invention.

It is convenient to combine the polyacetal polymer and filler according to a weight ratio determined by the respective densities thereof and the goal volume fraction of filler. The weight ratio is determined from the equation

25
$$W_f/W_p = [VF/(1-VF)] \cdot D_f/D_p$$

where W_f is the weight of the filler, W_p is the weight of the polymer, VF is the desired volume fraction of filler, in the range of about 0.01-0.3 as herein described, D_f is the density of the filler, and D_p is the density of the polymer. The density, D , is not the bulk density but the actual density of the material.

30 The present invention is further illustrated by the following specific embodiments which are not intended to be limiting thereon.

EXAMPLES

EXAMPLES 1-3 AND COMPARATIVE EXAMPLE A-J

In the following examples, Celcon® M270 polyacetal copolymer
35 (Hoechst-Celanese) was melt blended with the types and concentrations of CaCO_3 shown in Table 2. All the fillers were obtained from Specialty Minerals Inc. The three stearic acid treated fillers were similarly surface treated. Melt blending was accomplished in a 28 mm co-rotating twin screw extruder (Werner & Pfleiderer,

Ramsey, NJ) at barrel temperatures of 220°C . The extrudate was pelletized and the pellets were dried overnight at 60°C. The dried pellets were molded into test bars in a 6 oz., 150 ton Van Dorn injection molding machine equipped with a water-heated mold. The molding machine barrel temperatures were set at 220°C
5 and the mold temperature was set at 60°C.

In Comparative Example A, Celcon® M270 was extruded and injection molded without filler.

All compositions were molded into dog-bone shaped tensile bars for determination of Young's modulus according to ASTM D638-95 (Type I
10 specimen, 2" long gauge length; 1/2" wide; 1/8" thick) and flexural test bars (5" long, 1/2" wide, 1/8" thick) suitable for flexural testing according to ASTM D790 and for use in the notched Izod Impact Resistance test, ASTM D256. For Izod testing, the injection molded flexural test bars were divided into two 2-1/2" long pieces, one close to the gate and referred to as the "near end" and the other
15 far from the gate and referred to as the "far end". The results are shown in Table 2.

The data of Table 2 shows that both stiffness and impact resistance are simultaneously enhanced with filler particles within a range of about 0.1 to less than about 3.5 microns. Table 2 shows that at filler sizes below this range, of
20 0.07 μm , and at 3.5 μm the Izod values did not increase. In addition, the Izod values did not increase with the uncoated Albafil®

Table 2

	Filler in Celcon® M270	Stearic Acid Coated?	Av Particle Size (microns)	Vol %	Izod Impact (J/m) Near End	Izod Impact (J/m) Far End	Young's Mod (MPa)	Flexural Mod (MPa)
Comp. Ex. A				0	52.3	52.3	2852	2770
Comp. Ex. B	Ultra-Pflex®	Yes	0.07	5	46.5	52.3		
Comp. Ex. C	Ultra-Pflex®	Yes	0.07	10	32.0	32.0		
Comp. Ex. D	Ultra-Pflex®	Yes	0.07	20	32.0	32.0		
Example 1	Super-Pflex® 200	Yes	0.7	5	52.3	50.7	3094	3094
Example 2	Super-Pflex® 200	Yes	0.7	10	56.6	53.9	3734	3280
Example 3	Super-Pflex® 200	Yes	0.7	20	50.7	50.7	4368	3996
Comp. Ex. E	Albafil	No	0.7	5	46.5	50.7		
Comp. Ex. F	Albafil	No	0.7	10	46.5	46.5		
Comp. Ex. G	Hi-Pflex® 100	Yes	3.5	5	49.7	46.5		
Comp. Ex. H	Hi-Pflex® 100	Yes	3.5	10	48.1	49.7		
Comp. Ex. I	Hi-Pflex® 100	Yes	3.5	20	33.6	33.6		
Comp. Ex. J	Hi-Pflex® 100	Yes	3.5	25	32.0	32.0		

EXAMPLES 4,5 AND COMPARATIVE EXAMPLES K,L

Delrin® 500P polyoxymethylene homopolymer was processed in the manner of Examples 1-3 except that the extruder was a 30 mm twin screw extruder. Flexural modulus was determined according to ASTM D790. Only the flexural bar centers were used for the Izod test. Results are shown in Table 3.

Table 3: Polyoxymethylene homopolymer

Example	Filler	Stearic Acid Coated	Weight %	Flexural Modulus (MPa)	Izod, (J/m)
Comparative Example K				2917	80.1
Example 4	Super-Pflex® 200	Yes	10	3028	85.4
Comparative Example L				3117	69.4
Example 5	Super-Pflex® 200	Yes	10	3166	85.4

EXAMPLES 6-9 AND COMPARATIVE EXAMPLE M,N

The methods of Example 4 were employed except that the resin was a commercially available copolymer of polyoxymethylene incorporating 1 mol-% of ethylene oxide repeat units. The resin was characterized by a number average molecular weight of 28,300 Da and a weight average molecular weight of 99,200 Da, as determined by gel permeation chromatography following the general procedures outlined in ASTM D5296-92 employing hexafluoroisopropanol as the solvent. Results are shown in Table 4.

Table 4. Polyacetal Copolymer

Example	Filler	Stearic Acid Coated	Weight %	Flexural Modulus MPa	Izod, J/m
Comparative Example M				2352	69.4
Example 6	Super-Pflex® 200	Yes	10	2621	74.8
Example 7	Super-Pflex® 200	Yes	20	2828	80.1
Example 8	Super-Pflex® 200	Yes	30	3055	69.4
Example 9	Super-Pflex® 200	Yes	40	3779	53.4
Comparative Example N	Super-Pflex® 200	Yes	50	4566	42.7

CLAIMS

We claim:

1. A composition comprising a polyacetal polymer comprising polyoxymethylene and up to 10 mol-% of repeat units comprising oxyalkylene radicals having adjacent methylene units., about 1%-30% by volume of a mineral filler having an aspect ratio of 5 or less, the filler having an average equivalent spherical diameter in the range of about 0.1 to less than about 3.5 micrometers, and a saturated organic acid, salt thereof, or a mixture thereof, at a concentration of at least about 0.5% by weight of the mineral filler, said repeat units.
2. The composition according to Claim 1 wherein the composition comprises about 5-20% by volume of a mineral filler.
3. The composition according to Claim 1 wherein the composition comprises about 10-20% by volume of a mineral filler.
4. The composition of according to Claim 1 wherein the average equivalent spherical diameter is about 0.5 to about 2 micrometers.
5. The composition according to Claim 1 wherein the concentration of saturated organic acid, salt thereof, or mixture thereof is in the range of about 0.5-4%.
6. The composition according to Claim 1 wherein the saturated organic acid, salt thereof, or mixture thereof comprises one or more saturated fatty acids, salts thereof, or a mixture thereof.
7. The composition according to Claim 6 wherein the saturated fatty acid is stearic acid.
8. The composition according to Claim 4 wherein the saturated organic acid is stearic acid at a concentration of about 2% by weight on the weight of the filler.
9. The composition according to Claim 1 wherein the inorganic filler is calcium carbonate.
10. The composition of Claim 1 wherein the repeat units comprising oxyalkylene radicals having adjacent methylene units are ethylene oxide repeat units.
11. The composition of Claim 1 wherein the polyacetal polymer is a polyoxymethylene homopolymer.
12. A shaped article comprising the composition of Claim 1.
13. A process for forming a composition, comprising the steps of combining a polyacetal polymer comprising polyoxymethylene and up to 10 mol-% of repeat units comprising oxyalkylene radicals having adjacent methylene units, with a mineral filler having an aspect ratio of less than 5, the

mineral filler having an average equivalent spherical diameter in the range of about 0.1 to about 3.5 micrometers, and a saturated organic acid, salt thereof, or a mixture thereof, at a concentration of at least about 0.5% by weight of the mineral filler, the mineral filler and the polyacetal being combined at a weight ratio given
5 by the formula:

$$W_f/W_p = [VF/(1-VF)] \cdot D_f/D_p$$

where W_f is the weight of the filler, W_p is the weight of the polymer, VF is the desired volume fraction of filler, in the range of about 0.01-0.3, D_f is the density of the filler, and D_p is the density of the polymer;

10 heating the combination to a temperature above the melting point of the polyacetal to form a molten composition;

mixing the molten composition to provide a homogenous melt; and,
cooling the molten composition.

14. The process of Claim 13 wherein VF is in the range of about
15 0.10-0.20.

15. The process of Claim 13 wherein the average equivalent spherical diameter is about 0.5-2 micrometers.

16. The process of Claim 15 wherein the saturated organic acid, salt thereof, or mixture thereof comprises saturated fatty acids, salts thereof, or a
20 mixture thereof.

17. The process of Claim 15 wherein the saturated organic acid is stearic acid at a concentration of about 2% by weight on the weight of the filler.

18. The process of Claim 16 wherein the saturated fatty acid is stearic acid.

25 19. The process of Claim 13 wherein the inorganic filler is calcium carbonate.

20. The process of Claim 13 wherein the repeat units comprising oxyalkylene radicals having adjacent methylene units are ethylene oxide units.

21. The process of Claim 13 wherein the polyacetal polymer is a
30 polyoxymethylene homopolymer.

INTERNATIONAL SEARCH REPORT

International Application No

PC 1, US 00/22531

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L59/00 C08K13/02 C08K9/04 C08K5/09 C08K3/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 297 548 A (CELANESE CORP.) 22 November 1972 (1972-11-22) page 4, line 18 -page 5, line 12 ---	1
A	EP 0 340 931 A (POLYPLASTICS CO) 8 November 1989 (1989-11-08) claim 1 ---	1
X	GB 1 123 358 A (HOECHST AG) 14 August 1968 (1968-08-14) claim 1; table 1 ---	1-21
X	JP 01 170641 A (POLYPLASTICS CO) 5 July 1989 (1989-07-05) example 8 --- -/--	1-21

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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Date of the actual completion of the international search

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27/04/2001

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PC 17 US 00/22531

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 4 456 710 A (LUEDERS WALTER ET AL) 26 June 1984 (1984-06-26) claims 1-29</p> <p>-----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/22531

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